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EXAMINATION OF THE DISCHARGE MECHANISM OF LI/CF_x CELLS,
COMPARISON OF THE ELECTROCHEMICAL REDUCTION MECHANISMS
OF PTFE AND (CF_x)_n BY LITHIUM

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ABSTRACT

Swelling of $(CF_x)_n$ electrodes in commercial $Li/(CF_x)_n$ cells presents a limiting factor in cell design optimization. Examination of cathodes from such cells, after discharge, reveals a relation between cell operating temperatures and cathode swelling. Attempts to explain the swelling using the prevailing model for the cathode reaction have failed.

A more suitable reaction mechanism is proposed based on the observed behavior of $(CF_x)_n$ electrodes on discharge and a comparison of the reaction products of $(CF_x)_n$ and PTFE with lithium amalgams. The proposed mechanism is in agreement with the experimental data found in the literature.

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- o INTRODUCTION
- o TEARDOWNS OF COMMERCIAL CELLS
- o LITHIUM AMALGAM REACTIONS
- o DISCUSSION
- o REACTION MECHANISM
- o ONGOING WORK
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INTRODUCTION

Early developers of lithium-organic electrolyte cells were attracted to $(CF_x)_n$ as a potential cathode material. This attraction was based on calculated theoretical energy values of which the most outstanding was a theoretical specific energy approaching 2000 wh/kg*. Calculations of solid volume changes in the $Li/(CF_x)_n$ cells, based on "crystallographic" densities, indicated a volume reduction caused by active materials transforming into products of about 35%. However, in practice, loading of active materials was limited by an unexplained severe cathode swelling which resulted in cell choking and/or bulging of flat cell walls.

This investigation was aimed at trying to understand the cathode swelling phenomenon and, if possible, find a way to increase the active material loading in $Li/(CF_x)_n$ cells. The assumption that a "cure" might be found was based on the introduction of the solvated lithium ion "intercalation" model by Watanabe and coworkers in Japan**.

This presentation covers some of the results of the first three stages of this investigation: pre and post discharge teardowns of commercial cells, lithium amalgam reaction with $(CF_x)_n$, a discussion of results and postulation of a plausible reaction mechanism. Some comments regarding on-going work will also be made.

* This number is based on the assumption that the EMF of the electrochemical reaction is between 2.8 and 2.9 volts. See - J. P. Gabano, "An Overview" in "Lithium Batteries" (J. P. Gabano ed) P. 2, Academic Press, New York, NY, 1983.

** For a full presentation of Watanabe's group work see "Graphite Fluorides and Carbon-Fluorine Compounds", T. Nakajima and N. Watanabe, CRC Press, Boca Raton, FL, 1990.

VOLUME CHANGES OF CATHODES IN BR-2325 CELLS DUE TO DISCHARGE

WET CATHODES VOLUME BEFORE DISCHARGE

	Volume *(Cm ³)
PC/DME	0.261
GBL	0.251

CATHODES FROM DISCHARGED CELLS

32°F and 120°F Discharge Across a 37,500 ohm Load

Δ Volume* (%)

	<u>32°F</u>	<u>120°F</u>
PC/DME	36	1
GBL	36	2

75°F Discharge Across a 15,000 ohm Load

Δ Volume* (%)

PC/DME	27
GBL	28

* ± 1%

TEARDOWN OF COMMERCIAL CELLS

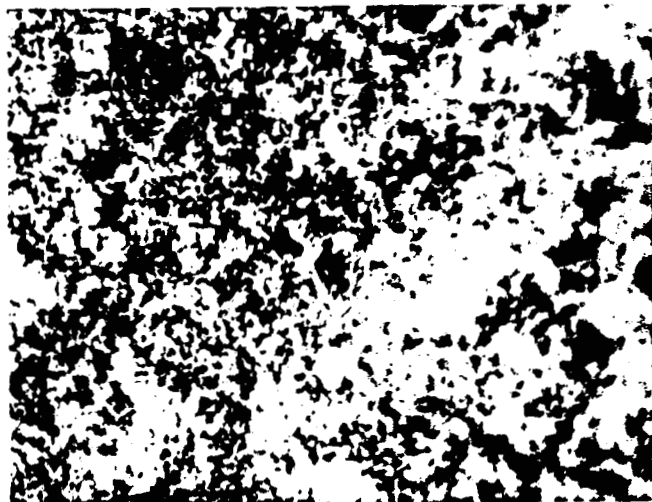
A number of commercial cells were torn down, pre and post discharge. In all cases significant cathode swelling was observed during discharge. For example, the cores of pin cells, which were easily removed from the cell can before discharge, could not be released without cutting the can, after discharge.

The most interesting observations were made in button cells where special provisions were made to accommodate cathode swelling.

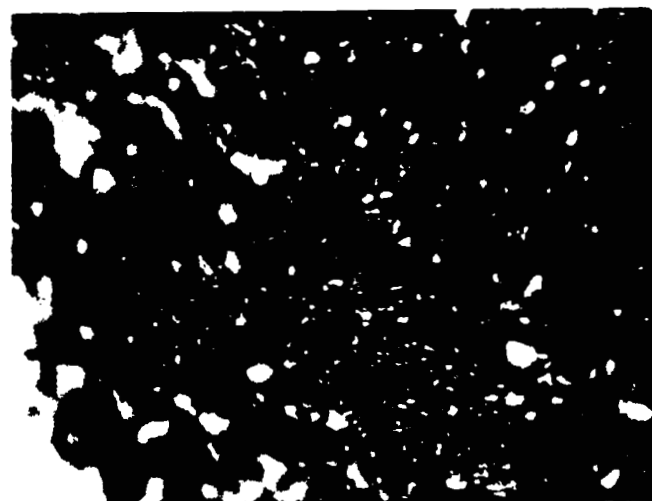
Most significant were results obtained from measurements of the dimensions of $(CF_x)_n$ cathodes from button cells before and after discharge at different temperatures, for example, the results obtained from BR2325 cells. Considering that manufacturer I used a propylene-carbonate (PC) - dimethoxyethane (DME) solutions and manufacturer II used a 4-butyrolactone (GBL) solution and that the obtained cell capacities were similar, one is hard pressed to claim a major impact of solution composition on swelling.

However, a clear trend regarding the degree of swelling and its relation to temperature and perhaps rate of discharge is apparent.

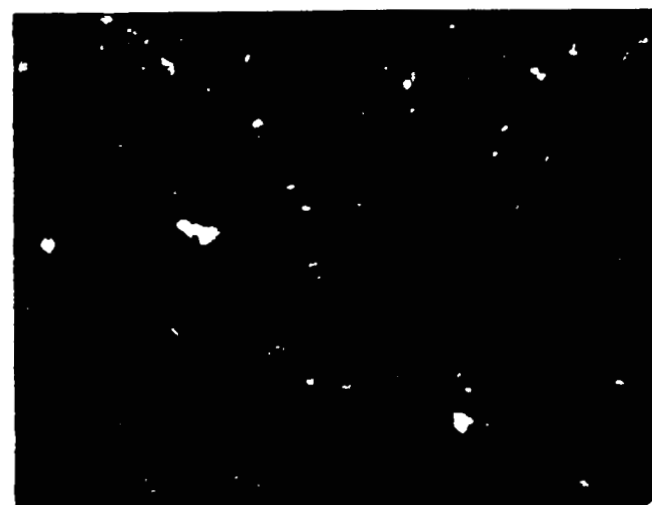
Original $(CF_x)_n$ Powder



RT Amalgam Reaction Product



60°C Amalgam Reaction Product



SEM MICROGRAPHS OF DISCHARGE PRODUCTS

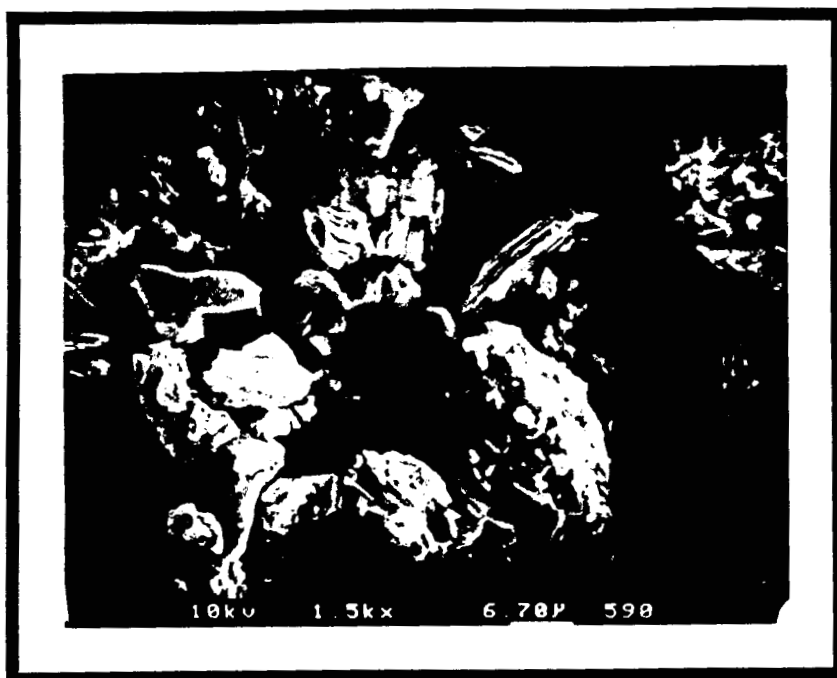


Original $(CF_x)_n$ Powder



60 C Amalgam Reaction Product

SEM MICROGRAPHS OF DISCHARGE PRODUCTS (Cont.)



RT Amalgam Reaction Product



RT Reaction Product From Li/1M LiAsF₆ in DMSI
(CF_x)_n Hg Cell

LITHIUM AMALGAM REACTIONS WITH $(CF_x)_n$

Dousek and coworkers have investigated the reaction of PTFE, a similar fluorocarbon, with lithium amalgams*. They reported that the reduction proceeded by lithium ions and electrons migration to C-F reaction sites through the polymer without involving the solvent.

Attempts to run a similar experiment by submerging $(CF_x)_n$ in a lithium amalgam failed. However, $(CF_x)_n$ powder spread over the amalgam surface, in a controlled atmosphere box under argon, started reacting and turning first gray and ultimately black at room temperature.

A similar experiment was run by placing $(CF_x)_n$ powder on the amalgam in a sealed vessel and storing it at 60°C.

The reaction products from both reactions were examined under the microscope and by SEM. The room temperature product consisted of a finer powder while the 60°C product appeared more coarse.

SEM micrographs of both reaction products showed opening of the $(CF_x)_n$ layers and small crystallites in the openings. It appears that more and bigger crystallites formed in the high temperature product. Note also the similarity between the SEM micrographs of $(CF_x)_n$ discharged, with Hg as a current collector and a 1M LiAsF₆ solution, vs lithium and the SEM micrograph for the room temperature amalgam reaction product.

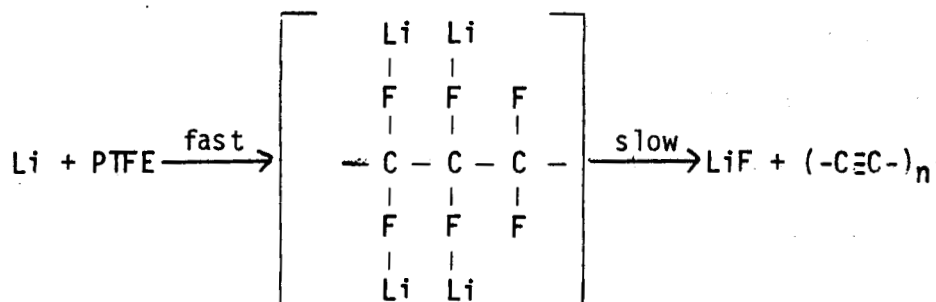
* Dousek and coworkers published a number of papers on this subject. Of particular interest should be:

1. F. P. Dousek and J. Jansta, *Electrochemical Acta*, 20, 1 (1975).
2. F. P. Dousek and J. Jansta, *Carbon*, 18, 13 (1980).
3. L. Kavan, F. P. Dousek, D. Micka and J. Weber, *Carbon*, 26, 235 (1988).

ELECTROCHEMICAL REDUCTION OF PTFE AND $(CF_x)_n$ BY LITHIUM

PROPOSED MECHANISMS

PTFE (Dousek et al)



$[-C\equiv C-]_n \longrightarrow$ to more ordered form

$LiF \longrightarrow$ to larger crystals

$(CF_x)_n$ by analogy



DISCUSSION

These results, the $\text{Li}/(\text{CF}_x)_n$ literature and Dousek's work on the electrochemical reduction of PTFE by lithium amalgam suggest that both fluorocarbons react similarly with lithium amalgams.

In the case of PTFE, lithium ions migrate through the solid, electrons migrate through the carbon chain, crystallites of LiF are formed and the carbon chains attempt to form carbon rings if not small graphene layers. X-ray diffraction indicates the presence of LiF but "no carbon". Active carbon released by room temperature removal of the LiF is soft and springy. When LiF is released by melting, the remaining carbon is more coarse. Most noteworthy are the observations that:

- Resistivity measurements on PTFE reaction products indicate an exponential decline still measureable about a year after the material was formed.
- The rate of LiF crystal growth and decreasing resistivity are also temperature dependent.

A similar mechanism can be proposed for the cathode reaction in $\text{Li}/(\text{CF}_x)$ cell assuming that the chemical step following the electrochemical step is also slow.

MARGRAVE

THERMODYNAMIC AND E^0 VALUES FOR THE REACTION
 $XnLi + (CF_x)_n \rightarrow XnLiF + xnC$

THERMODYNAMIC AND E^0 VALUES FOR EQUATION

X in CF	$-\Delta G^0_{298}$ kJ/mole	$-\Delta S^0_{298}$ J/mole K	E^0 Volts
0.8	378.2	7.57	4.90
0.9	413.8	8.51	4.76
1.0	499.4	9.46	4.66

EBEL AND KIESTER

HEAT RELEASED BY NON-ELECTROCHEMICAL PROCESS

<u>Current</u>	<u>KJ/mol*</u>
50 μA	120
150 μA	110
300 μA	100
0 μA^{**}	135

* Estimated from graph

** Extrapolated

Such a mechanism could explain the apparent "anomaly" reported by Ebel and Keister regarding the heat released by a $\text{Li}/(\text{CF}_x)_n$ cell due to non electrochemical process(es) during discharge*. They reported that the heat per mole evolved by such process(es) increased as the current decreased approaching a value predicted on the basis of Margrave's thermodynamic calculations**. As their currents went down to values below 50 A one could assume that they were discharging their cell slow enough so that a significant amount of the forming intermediate decomposed during discharge. As the rate of discharge increased, less heat per mole was generated by these processes during discharge.

The slow decomposing intermediate model also helps in understanding how cells survive relatively high rate discharges and are not destroyed by the amount of heat which must be released by the non electrochemical processes.

The implication of this proposed reaction mechanism in terms of heat management and preferred discharge regimes are interesting but go beyond the scope of this presentation.

Still X-ray diffraction does not show the presence of a $[\text{CFLi}]$ entity on the surface of the discharge product composite neither in the case of $(\text{CF}_x)_n$ nor in the case of PTFE. The question remains, how does the lithium ion reach C-F reaction sites in both cases after the intermediate on surface layer has decomposed.

* S. J. Ebel and P. Keister in "Proceeding of the Electrochemical Society Meeting" Las Vegas, October 1985, Abstract 91.

** For a detailed account of Margrave's work see - J. L. Wood, A. J. Valerga, R. B. BaLachope, and J. L. Margrave. ECOM-0105F (AD 755934), Final Report, December 1972.

PROPOSED MECHANISM

- STEP 1: Lithium ion enters through carbon.
- STEP 2: Lithium ion reaches C-F reaction site.
- STEP 3: Intermediate formation.
- STEP 4: Intermediate decomposition.
- STEP 5: Growth of LiF crystallites and ordering of carbon.

PROPOSED MECHANISM

We propose that after the surface of the fluorocarbon is covered with carbon and LiF, lithium ions proceed to enter the composite solid reaction product through the carbon. Indeed the more ordered the product carbon is the faster lithium ions should migrate through it, hence, the preference for relatively ordered carbons for the production of $(CF_x)_n$.

Electrons entering through the carbon skeleton and lithium ions migrating through the carbon can reach reaction sites and form the intermediate.

The intermediate will decompose into carbon and LiF at a rate depending on temperature. The nature of the resultant composite, i.e. size of LiF crystallites and the degree of order of the carbon, will depend on the temperature history of the reaction and the stored reaction product.

ONGOING WORK

1. Testing the "lithium moving through carbon" hypothesis.
2. Examining $(CF_x)_n$ powder discharged at different temperatures.
3. Starting to look for "post discharge" heat generation.

CONCLUSION

- o It appears that cathode swelling in $\text{Li}/(\text{CF}_x)_n$ cells is a result of changes in particles morphology during discharge.
- o Electrodes swelling, at least in commercial button cells, appears to be temperature dependent.
- o The postulated mechanism seems to explain available data.
- o The challenge remains - can the swelling of $(\text{CF}_x)_n$ cathodes during discharge be reduced so as to allow significantly better performance of $\text{Li}/(\text{CF}_x)_n$ cells.